ARTICLES

Synthesis and photovoltaic properties of low bandgap dimeric perylene diimide based non-fullerene acceptors

Xin Zhang, Jiannian Yao & Chuanlang Zhan^{*}

Beijing National Laboratory of Molecular Science; Key Laboratory of Photochemistry, Chinese Academy of Sciences; Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Received June 9, 2015; accepted July 6, 2015; published online October 22, 2015

Non-fullerene organic acceptors have attracted increasing attention in recent years. One of the challenges in the synthesis of non-fullerene organic acceptors is to tune the absorption spectrum and molecular frontier orbitals, affording low bandgap molecules with improved absorption of the near-infrared solar photons. In this paper, we present the synthesis, optoelectronic and photovoltaic properties of a series of dimeric perylene diimide (PDI) based non-fullerene acceptors. These PDI dimers are bridged by oligothiophene (T) from **1T** to **6T**. With the increase of the oligothienyl size, the highest occupied molecular orbital (HOMO) energy is raised from -5.65 to -5.10 eV, while that of the lowest unoccupied molecular orbit (LUMO) is kept constant at -3.84 eV, affording narrow bandgap from 1.81 to 1.26 eV. The absorption from the oligothiophene occurs between 350 and 500 nm, which is complementary to that from its bridged PDI units, leading to a wide spectral coverage from 350 to 850 nm. The optimal dihedral angle between the bridged two perylene planes is dependent on the oligothienyl size, varying from 5° to 30°. The solubility of the dimers depends on the oligothienyl size and can be tuned by the alkyl chains on the bridged thienyl units. The possible applications as the solution-processable non-fullerene organic acceptor is primarily studied using commercial P3HT as the blend donor. The photovoltaic results indicate that **1T**, **4T** and **6T** all yield a higher efficiency of ~1.2%, whereas **2T**, **3T** and **5T** all give a lower efficiency of <0.5%. The difference in the cell performance is related with the tradeoff between the differences of absorption, HOMO level and film-morphology between these dimers.

non-fullerene acceptor, organic photovoltaic cell, perylene diimide, solution-processed, bulk-heterojunction

Citation: Zhang X, Yao JN, Zhan CL. Synthesis and photovoltaic properties of low bandgap dimeric perylene diimide based non-fullerene acceptors. *Sci China Chem*, 2016, 59: 209–217, doi: 10.1007/s11426-015-5485-8

1 Introduction

Non-fullerene organic photovoltaic (OPV) cells use nonfullerene organic n-type molecule (small or polymeric) as the acceptor, which is blended with small molecule or polymer donor to form the photoactive blend layer. In 1986, Tang [1] used a phthalocyanine compound as the donor (D) and a perylene diimide (PDI) derivative as the acceptor (A), proposing the first OPV cell with a bilayered planar cell structure. Since then, a number of organic acceptors have been synthesized, for example, 9,9'-bifluorenylidene [2], benzothiadiazole [3,4], naphthalene diimide [5–8], quinacridone [9], fluoranthene-fused imide [10,11], decacyclene triimide [12], diketopyrrolopyrrole [13], electron-deficient pentacene [14], and indandione [15].

In 2013, the effort leads to significant advances. Because the PDI chromophore exhibits promising optoelectronic attributes such as strong absorption in the visible region of 450 to 650 nm [16], good electron affinity with tunable low-lying lowest unoccupied molecular orbital (LUMO, about -4.0 eV) [17], high electron mobility of 10^{-3} -10 cm²/(V s) [18], and high chemical, thermal, and photochemical stabilities [19], it is considered as a potential can-

^{*}Corresponding author (email: clzhan@iccas.ac.cn)

[©] Science China Press and Springer-Verlag Berlin Heidelberg 2015

didate of n-type organic semiconducting moieties to synthesize non-fullerene organic acceptors. However, the key factor that limits its applications in OPVs is the aggregation tendency, which is caused by the large π -system of the perylene core. When blended with a donor, PDI acceptor often forms large aggregates, typically with a size of over 100 nm, severely limiting the charge-dissociation [20]. After reduction of the aggregation tendency by the formation of twisted dimeric [21-28] or trimeric [29,30] backbone, or by imidization using branched alkyl amine such as 1-ethylpropylamine [31-33] or by incorporation of large conjugated π -systems, for example, on the bay region [34], the power conversion efficiency (PCE) from the PDI based small molecule acceptors has been raised up to 3%-4% [21–26]. With respect to the conventional cell configuration, an inverted cell structure takes advantages of the carrierextraction favourable donor/acceptor (D/A) distribution in the top and buried surface of the active layer, which leads to a higher PCE value (4.34% vs. 3.28%) [35]. On another aspect, the inverted cell structure can trap more light and a PCE of 5.9% was achieved by using an inverted cell structure with a fullerene self-assembled monolayer (C_{60} -SAM) on the ZnO electron selective layer [36]. Very recently, the PCE value from the small molecule acceptor based nonfullerene OPVs has been increased up over 6% either from perylene derivatives or other n-type small molecule semiconductors [37-40].

With respect to the fullerene acceptor, organic counterpart normally shows absorption in the visible region of wavelength. Generation and consequent exploitation of the acceptor's excitons is thus the same important as the donor's for efficient non-fullerene solar cells. This requires improving the light harvesting ability. Moreover, this requires the acceptor molecule having suitable HOMO level to match with that of the blend donor, affording efficient hole transfer from the acceptor to the blend donor. Accordingly, it is an issue in the research of non-fullerene solar cells to tune the light-harvesting ability and the HOMO energy level of the organic acceptor via the backbone modifications.

In this paper, we report a series of PDI dimer based acceptors (Figure 1), in which the absorption and HOMO



Figure 1 Molecular structures of the six PDI dimers.

level are both tuned simply by the size of the bridged oligothiophene. The photovoltaic properties of these organic acceptors are primarily checked by using the commercial P3HT as the blend donor.

2 Experimental

2.1 Materials and instruments

The polymer of P3HT was purchased from Solarmer company. ¹H NMR and ¹³C NMR spectra were recorded by a Bruker DMX-400 (Germany) spectrometer with CDCl₃ as a solvent and tetramethylsilane as an internal reference. MALDI-TOF mass spectra were recorded by a Bruker BIFLEXIII (Germany). Transmission electron microscopy (TEM) tests were performed on a JEM-2011F (JEOL, Japan) which is operated at 200 kV. The cyclic voltammetry (CV) was performed using a Zahner IM6e electrochemical workstation in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) dichloromethane (DCM) solution with a scan speed at 0.1 V/s. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The concentration of the dimer is 1×10^{-4} mol/L in chromatographic pure DCM. Absorption spectrum was measured on Hitachi U-3010 (Japan) UV-Vis spectrophotometer. All spectroscopic measurements were carried out at room temperature. The film spectrum was obtained via the transmission mode. The thickness of the solid films was measured by Bruker Dektak XT Profilometer (USA). Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 (USA) at a heating rate of 10 °C/min under nitrogen flow.

2.2 Measurements of solubility

A working plot was first built for each dimer by plotting the absorbance at 560 nm versus concentration, which is controlled from 1×10^{-6} to 1×10^{-5} mol/L. Secondly, a saturated solution was prepared for each dimer at room temperature and it was then diluted to this concentration range. The real concentration of this dilute solution was estimated according to its absorbance, from which the solubility was finally measured.

2.3 Quantum chemical calculations

Density functional theory calculations were performed with the Gaussian 09 program, using the B3LYP functional. All-electron double- ξ valence basis sets with polarization functions 6-31G* were used for all atoms. Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects. Vibrational frequency calculations were performed to check that the stable structures had no imaginary frequency.

2.4 Fabrications and characterizations of organic solar cells

Solar cell devices with a typical configuration of ITO/ PEDOT:PSS/active layer/Ca/Al was fabricated as follows: The ITO glass was pre-cleaned with deionized water, CMOS grade acetone and isopropanol in turn for 15 min. The organic residues were further removed by treating with UV-ozone for 1 h. Then the ITO glass was modified by spin-coating PEDOT:PSS layer (30 nm) on it. After dried in oven at 150 °C for 15 min, the active layer was spin-coated on the ITO/PEDOT:PSS surface with a blend solution of PDI dimer and P3HT (40 mg/mL in o-DCB). The electrode with Ca (20 nm) and Al (80 nm) was then thermally evaporated onto the active layer under the vacuum of 1×10^{-4} Torr. The active area of the device was 0.06 cm^2 , and the thicknesses of the active films were ~100 nm. The devices were characterized in nitrogen atmosphere under the illumination of simulated AM 1.5 G, 100 mW/cm² using a xenon-lampbased solar simulator (AAA grade, XES-70S1). The current-voltage (J-V) measurement of the devices was conducted on a computer-controlled Keithley 2400 Source Measure Unit. The external quantum efficiency (EQE) measurements were performed in air using QE-R3011 (Enli Technology Co. Ltd., Taiwan, China) with a scan increment of 10 nm per point.

2.5 Mobility measurements by space-charge limited current (SCLC) method

The electron-only devices were fabricated with a configuration of ITO/titanium (diisopropoxide) bis(2,4-pentanedionate) [41] (TIPD, 20 nm)/blend (150 nm)/Al (100 nm). Since the HOMO and LUMO energy levels of TIPD are of -3.91 and -6.0 eV, respectively, it can be used to fabricate the electron-only SCLC device. The TIPD buffer layer was prepared by spin-coating a 3.5 wt% TIPD isopropanol solution onto the pre-cleaned ITO substrate and then baked at 150 °C for 10 min to convert TIPD into TOPD. Subsequently, the blend was spin-coated on it under the same condition as preparation of the optimal solar cell. The Al layer was thermally deposited on the top of the blend in vacuum. The Al layer was deposited at a speed of 1 Å/s. The electron mobility was extracted by fitting the current density-voltage curves using the equation $J=9/8\varepsilon\varepsilon_0\mu_h V^2/L^3$ $\times \exp[0.89(V/E_0L)^{0.5}]$ [42], where ε is the dielectric constant of the polymer (here, 3 is used), ε_0 is the permittivity of the vacuum (8.85419×10⁻¹² CV⁻¹ m⁻¹), μ_h is the zero-field mobility, E_0 is the characteristic field, J is the current density, L is the thickness of the films, and $V=V_{appl}-V_{bi}$, here V_{appl} is the applied potential, and $V_{\rm bi}$ is the built-in potential which results from the difference in the work function of the anode and the cathode (in the electron-only device, $V_{\rm bi}=0$ V). The electron mobility of the solar cell blend is deduced from the intercept value of $\ln(9\varepsilon\varepsilon_0\mu_0/8)$ by linearly plotting $\ln(JL^3/V^2)$ vs. $(V/L)^{0.5}$.

2.6 General procedure for synthesis of 2d–2f

A mixture of 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiophene (5, 492.4 mg, 1.00 mmol) and 2-tributylstannylthiophene (6, 821.0 mg, 2.20 mmol) was dissolved in dry toluene (20 mL). A catalytic amount of $Pd[P(C_6H_5)_3]_4$ (69.3 mg, 0.06 mmol) was added and the reaction mixture was stirred at 110 °C for 36 h. The mixture was extracted with dichloromethane (DCM) and then washed with water. Then the DCM layer was dried over Na₂SO₄. After removal of DCM, the residue was subjected to chromatography with petroleum ether/ DCM as eluents to afford 3',4"-dihexyl-2,2':5',2":5",2"'quaterthiophene (2d) (399.1 mg, 0.80 mmol, 80%) as a yellow solid; ¹H NMR (400MHz, CD_2Cl_2) δ ppm: 7.32 (d, J=5.20 Hz, 2H), 7.14 (m, 2H), 7.07 (m, 2H), 7.02 (s, 2H), 2.72 (t, J=8.00 Hz, 4H), 1.65 (m, 4H), 1.38 (m, 4H), 1.31 (m, 8H), 0.88 (t, J=6.76 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 140.5, 136.1, 135.1, 129.7, 127.6, 126.5, 126.0, 125.5, 31.8, 30.7, 29.5, 29.4, 22.8, 14.2; TOF MS: $m/z=499.2 [M+H]^+$.

3"-Hexyl-2,2':5',2":5",2"':5"',2""-quinquethiophene (**2e**). The general procedure was followed, and flash column chromatography (silica gel, petroleum ether/DCM) afforded **2e** (372.1 mg, 0.75 mmol, 75%) as a yellow solid; ¹H NMR (400 MHz, CD₂Cl₂) δ ppm: 7.24 (m, 2H), 7.20 (m, 2H), 7.13 (s, 1H), 7.08 (m, 2H), 7.04 (m, 4H), 2.76 (t, *J*=8.00 Hz, 2H), 1.66 (m, 2H), 1.39 (m, 2H), 1.31 (m, 4H), 0.88 (t, *J*=6.76 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 140.6, 137.3, 137.2, 137.2, 136.3, 136.0, 134.9, 129.6, 128.0, 126.7, 126.4, 124.6, 124.5, 124.3, 124.1, 123.8, 123.7, 31.8, 30.6, 29.6, 29.4, 22.8, 14.2; TOF MS: *m/z*=497.1 [M+H]⁺.

3",4"'-Dihexyl-2,2':5',2":5",2"':5"',2"":5"",2""'-sexithiophene (**2f**). The general procedure was followed, and flash column chromatography (silica gel, petroleum ether/DCM) afforded **2f** (496.6 mg, 0.75 mmol, 75%) as an orange solid; ¹H NMR (400MHz, CD₂Cl₂) *δ* ppm: 7.23 (dd, *J*=0.88, 4.88 Hz, 2H), 7.20 (dd, *J*=0.90, 3.48 Hz, 2H), 7.13 (d, *J*=3.76 Hz, 2H), 7.04 (m, 4H), 7.00 (s, 2H), 2.77 (t, *J*=8.00 Hz, 4H), 1.70 (m, 4H), 1.43 (m, 4H), 1.36 (m, 8H), 0.93 (t, *J*=6.76 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) *δ* ppm: 140.6, 137.2, 137.1, 135.1, 135.0, 129.6, 128.0, 126.7, 126.5, 124.6, 124.1, 123.8, 31.8, 30.6, 29.7, 29.4, 22.8, 14.3; TOF MS: *m*/*z*=663.1 [M+H]⁺.

2.7 General procedure for synthesis of 3a–3f

A solution of *n*-BuLi (2.20 mol/L in hexane, 1.00 mL, 2.20 mmol, 2.20 equiv.) was added dropwise to a solution of **2a** (68.1 mg, 1.00 mmol, 1.00 equiv.) in anhydrous tetrahydrofuran (THF, 15 mL) in a Schlenk flask at -78 °C. After 1 h at -78 °C, the reaction mixture was stirred at ambient temperature for 30 min. Then, Me₃SnCl (1.00 mol/L in THF, 2.50 mL, 2.50 mmol, 2.50 equiv.) was added and the stirring was maintained for 1 h. After dilution with ethyl acetate (EtOAc, 50 mL), the mixture was washed with a saturated aqueous solution of KF (20 mL) and then water, dried over MgSO₄ and solvent was removed by distillation under vacuum. The residue was recrystallized from methanol to give 2,5-bis(trimethylstannyl)thiophene (**3a**) (369.8 mg, 0.90 mmol, 90%) as a white crystal.

5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (**3b**). **3b** (442.7 mg, 0.90 mmol, 90%) was recrystallized from methanol as a white flake crystal.

5,5"-Bis(trimethylstannyl)-2,2':5',2"-terthiophene (3c). 3c (528.1 mg, 0.92 mmol, 92%) was recrystallized from methanol as a pale yellow needle crystal.

5,5"'-Bis(trimethylstannyl)-3',4"-dihexyl-2,2':5',2":5",2"'quaterthiophene (**3d**). **3d** (750.2 mg, 0.91 mmol, 91%) was recrystallized from methanol as a yellow needle crystal.

5,5""-Bis(trimethylstannyl)-3"-hexyl-2,2':5',2":5",2"':5"', 2""-quinquethiophene (**3e**). **3e** (674.4 mg, 0.82 mmol, 82%) was recrystallized from methanol as a yellow needle crystal.

5,5'''-bis(trimethylstannyl)-3'',4''-dihexyl-2,2':5',2'':5'',2'':5'',2'':5''',2''':5''',2''''-sexithiophene (**3f**). **3f** (840.4 mg, 0.85 mmol, 85%) was recrystallized from methanol as a yellow needle crystal.

2.8 General procedure for synthesis of PDI dimers 1 from 2T to 6T

The synthetic procedure is similar to that of bis-PDI-T-EG (**1T**), that we have previously reported [21,22].

2T was got in a yield of 83%. ¹H NMR (400 MHz, CDCl₃) δ ppm: 9.59–9.45 (m, 2H), 8.80–8.11 (m, 10H), 7.22–7.11 (m, 4H), 4.72–4.55 (m, 4H), 4.23–4.04 (m, 8H), 4.04–3.95 (m, 4H), 3.66–3.55 (m, 6H), 2.04–1.84 (m, 4H), 1.48–1.19 (m, 32H), 1.02–0.80 (m, 24H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 164.1, 164.0, 163.7, 163.6, 157.1, 144.0, 139.1, 135.4, 134.3, 133.5, 133.3, 133.2, 131.7, 131.5, 130.4, 129.4, 128.8, 128.7, 128.2, 127.9, 127.8, 125.9, 124.0, 123.7, 122.3, 121.8, 121.5, 120.8, 117.8, 70.9, 69.5, 59.6, 44.6, 38.2, 30.9, 28.9, 24.2, 23.2, 14.3, 10.8; Elemental analysis for C₉₄H₉₈N₄O₁₂S₂: Calcd. C, 73.32; H, 6.41; N, 3.64; S, 4.16; Found C, 72.95; H, 6.37; N, 3.67; S, 4.16. TOF MS: *m*/*z*=1539.6 [M+H]⁺.

3T was got in a yield of 85%. ¹H NMR (400 MHz, CDCl₃) δ ppm: 9.62–9.41 (m, 2H), 8.70–8.16 (m, 10H), 7.23–7.17 (s, 2H), 7.16–7.05 (m, 4H), 4.70–4.56 (m, 4H), 4.24–4.05 (m, 8H), 4.05–3.95 (m, 4H), 3.69–3.54 (m, 6H), 2.04–1.82 (m, 4H), 1.49–1.14 (m, 32H), 1.04–0.71 (m, 24H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 163.8, 163.6, 163.5, 157.0, 143.3, 139.5, 136.2, 135.1, 134.1, 133.3, 133.0, 132.2, 131.6, 131.4, 130.2, 129.3, 128.7, 128.5, 128.0, 127.8, 127.6, 125.3, 125.2, 123.9, 123.6, 122.2, 121.8, 121.5, 121.3, 120.6, 117.6, 70.9, 69.4, 59.6, 44.5, 44.4, 38.1, 31.0, 28.9, 24.2, 23.2, 14.3, 10.8; Elemental

analysis for $C_{94}H_{98}N_4O_{12}S_2$: Calcd. C, 72.57; H, 6.21; N, 3.45; S, 5.93; Found C, 72.75; H, 6.17; N, 3.47; S, 5.92. TOF MS: m/z=1622.1 [M+H]⁺.

4T was got in a yield of 85%. ¹H NMR (400 MHz, CD₂Cl₂) *δ* ppm: 9.49–9.32 (m, 2H), 8.57–8.02 (m, 10H), 7.18–6.99 (m, 6H), 4.67–4.52 (m, 4H), 4.15–3.93 (m, 12H), 3.68–3.54 (m, 6H), 2.77–2.62 (m, 4H), 1.96–1.81 (m, 4H), 1.71–1.57 (m, 4H), 1.45–1.16 (m, 44H), 0.98–0.84 (m, 24H), 0.84–0.69 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) *δ* ppm: 164.0, 163.6, 163.5, 157.0, 143.9, 141.3, 138.8, 135.4, 134.1, 133.2, 131.8, 129.3, 127.7, 127.0, 123.8, 122.1, 121.4, 117.5, 70.9, 69.4, 59.6, 44.6, 38.2, 31.7, 31.0, 30.4, 29.8, 29.3, 29.0, 28.9, 24.3, 23.3, 22.7, 14.3, 14.2, 10.8, 10.8; Elemental analysis for C₁₁₄H₁₂₆N₄O₁₂S₄: Calcd. C, 73.12; H, 6.78; N, 2.99; S, 6.85; Found C, 72.98; H, 6.76; N, 3.00; S, 6.86. TOF MS: *m/z*=1872.2 [M+H]⁺.

5T was got in a yield of 81%. ¹H NMR (400 MHz, CD₂Cl₂) δ ppm: 9.47–9.18 (m, 2H), 8.51–7.92 (m, 10H), 7.22–6.99 (m, 9H), 4.67–4.50 (m, 4H), 4.14–3.84 (m, 12H), 3.69–3.56 (m, 6H), 2.81–2.65 (m, 2H), 1.95–1.74 (m, 4H), 1.74–1.58 (m, 2H), 1.45–1.16 (m, 38H), 0.96–0.78 (m, 27H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 163.8, 163.6, 163.4, 156.9, 143.0, 139.7, 135.7, 134.0, 133.2, 132.4, 131.7, 130.2, 129.2, 128.7, 127.5, 124.5, 123.8, 123.5, 122.1, 121.3, 120.5, 117.5, 70.9, 69.4, 59.5, 44.6, 38.1, 31.8, 31.0, 30.5, 29.4, 28.9, 24.2, 23.3, 23.2, 22.8, 14.3, 10.8; Elemental analysis for C₁₁₂H₁₁₆N₄O₁₂S₅: Calcd. C, 71.92; H, 6.25; N, 3.00; S, 8.57; Found C, 71.58; H, 6.26; N, 3.01; S, 8.56. TOF MS: *m/z*=1870.7 [M+H]⁺.

6T was got in a yield of 75%. ¹H NMR (400 MHz, CD₂Cl₂) δ ppm: 9.41–9.22 (m, 2H), 8.49–7.96 (m, 10H), 7.21–6.84 (m, 10H), 4.65–4.47 (m, 4H), 4.15–3.86 (m, 12H), 3.70–3.54 (m, 6H), 2.81–2.60 (m, 4H), 1.93–1.75 (m, 4H), 1.75–1.58 (m, 4H), 1.45–1.16 (m, 44H), 0.98–0.73 (m, 30H); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 163.9, 163.6, 163.4, 156.9, 143.0, 140.8, 135.9, 135.1, 134.0, 133.0, 131.7, 129.5, 129.2, 128.5, 126.7, 124.8, 123.8, 123.5, 122.1, 121.3, 120.5, 117.4, 70.9, 69.3, 63.6, 59.6, 58.4, 38.2, 31.8, 30.9, 30.5, 29.8, 29.4, 28.9, 24.2, 23.2, 22.8, 14.3, 10.8; Elemental analysis for C₁₂₂H₁₃₀N₄O₁₂S₆: Calcd. C, 71.94; H, 6.43; N, 2.75; S, 9.45; Found C, 72.18; H, 6.45; N, 2.74; S, 9.45. TOF MS: *m/z*=2036.2 [M+H]⁺.

3 Results and discussion

3.1 Synthesis

As shown in Scheme 1, the distannyl product of thiophene (**3a**), bithiophene (**3b**) and trithiophene (**3c**) was synthesized from commercial oligothiophenes involved no alkyl side chains. Solubility of oligothiophene decreases with the size. To possibly increase solubility of synthesized PDI dimers, we introduced one or two *n*-hexyl side chains onto the β -position of the central thiophene on quaterthiophene,



Scheme 1 Synthetic procedure of oligothiophenes 2d–2f, and bis(trime-thylstannyl)oligothiophenes 3a–3f. Reagents and conditions: i) *n*-BuLi, THF, -78 °C; Me₃SnCl, r.t.; ii) 1% PdCl₂(PhCN)₂, AgNO₃/KF, DMSO, 60 °C; iii) 3% Pd(PPh₃)₄, toluene, 110 °C; iv) NBS, CHCl₃, 0 °C.

quinquethiophene, and sexithiophene. The palladiumcatalyzed C-H homocoupling reaction of the commercial 4 gave 5 in the presence of silver(I) nitrate and potassium fluoride at 60 °C for 6 h in 96% yield. Then, 2d was synthesized through a Stille coupling reaction between 5 and the commercial 6 in a yield of 80%. 8 was prepared by the dibromination of the commercial 7 under mild conditions with *N*-bromosuccinimide (NBS) in nearly quantitative yield. Palladium-catalyzed Stille coupling reaction of 8 with 9, and 5 with 9 yielded 2e and 2f, respectively. Stannylation of 2a-2f, respectively, afforded 3a-3f in 82%–92% yield.

Stille coupling between the bis(trimethylstannyl)oligothiophene and 1-(2-methoxyethoxyl)-7-brominated PDI (10) gave the target products of the perylene diimide dimers of 1T–6T, as shown in Scheme 2. Because PDI 10 was synthesized from 1,7-dibrominated PDI by following the nucleophilic substitution of one of the two bromo atoms [43], the product of PDI 10 will be certainly a mixture containing the unsymmetrically substituted 1-(2-methoxyethoxyl)-6brominated PDI as the minor component [44]. The 1,6- and 1,7-isomers are difficult to be separated, and, therefore each final compound of 1T–6T is surely a mixture, coupling from the 1,6- and 1,7-isomers [21,22]. The peaks appearing around 9.3 ppm in the ¹H NMR spectrum of each product of 4T–6T are indicative of the 1,6-isomers. Indeed, the product of 1T–3T also contains the components from the 1,6-



Scheme 2 Synthesis of dimeric PDIs 1T-6T bridged with oligothiophenes with 1-6 monomer units. Reagents and conditions: i) 3% Pd(PPh₃)₄, toluene, 110 °C.

isomers. However, the perylene-H atoms from the 1,6- and 1,7-isomers overlap around 9.5 ppm. Therefore, a broad band is seen in this position in the ¹H NMR spectrum of each product of 1T-3T.

3.2 Thermostability

Thermal stability of each dimer was investigated with thermogravimetric analysis (TGA) under a nitrogen atmosphere, as outlined in Figure S1 (Supporting Information online). The results reveal that these dimeric PDIs have excellent thermal stabilities with thermal decomposition temperatures ($T_{\rm d}$, 5% weight loss) over 400 °C.

3.3 Solubility

All dimers are soluble in the commonly used solvents such as 1,2-dichlorobenzene (*o*-DCB). The solubility in *o*-DCB is measured by spectrophotometric method and the results are collected in Table 1. The solubility is of ~30 mg/mL for **1T** and about 20 mg/mL for **2T**, **4T**, and **6T**, while reduces down to about 9 mg/mL for **3T** and **5T**. The higher solubility of **4T** and **6T** than **3T** is due to the introduction of soluble alkyl chains on the bridged thiophene units.

3.4 Molecular modeling

The optimal conformations of the dimers were calculated on Gaussian 09 at the B3LYP/6-31G level of theory in the gas phase. Figures 2 and S2 collect the optimal conformations and dihedral angles of the six PDI dimers. The dihedral angle between two PDI planes varies as the change of the bridge size. As indicated from Table 1, the dihedral angle between the two covalent PDI units increases slightly from 20.5° to 22.9° and 30.3° with the thienyl going from **1T** to **3T** and **5T**, while from **2T** to **4T** and **6T**, that value goes from 5.7° to 17.7° and 30.0° . The dihedral angle between the PDI plane and the directly attached thienyl plane is 50°

PDI	Solubility (mg/mL) ^{a)}	θ (°) ^{b)}	HOMO (eV)	LUMO (eV)	$E_{\rm g}^{\rm cv}$ (eV)
1T	28.0	20.49	-5.65	-3.84	1.81
2 T	19.3	5.66	-5.54	-3.84	1.70
3 T	8.5	22.87	-5.36	-3.84	1.52
4 T	21.6	17.72	-5.24	-3.84	1.40
5 T	9.8	30.33	-5.23	-3.84	1.39
6T	18.3	30.03	-5.10	-3.84	1.26

Table 1 Solubility, conformations and energy levels of the six dimers

a) Measured in o-DCB; b) dihedral angle between two PDI plane.



Figure 2 Optimal conformations of PDI dimers of 1T (a), 2T (b), 3T (c), 4T (d), 5T (e), 6T (f).

for all the six dimers. The dihedral angles between the two naphthalene planes of one PDI unit are of 20° and 15° , respectively, along the side attached to the bridged oligothienyl and along the other side attached with the 2-methoxylethoxyl unit. Otherwise, the oligothineyl twists in a different way with the increase of the size. This means that the increase of the size varies the twisted nature of the covalently linked two PDI units and also changes the coplanarity of the oligothienyl bridge.

3.5 Electrochemical properties

The electrochemical properties of the dimers were analyzed by using cyclic voltammetry (CV) with Ag/AgCl as reference electrode, as shown in Figure 3(a). The energy levels of the HOMO and LUMO were determined from the onset of oxidation and reduction waves, respectively, by using an offset of 4.40 eV for the Ag/AgCl versus the vacuum level (Table 1). Figure 3(b) depicts the energy level diagrams of the synthetic PDIs, P3HT [21], and PC₆₁BM. The HOMO level is raised from -5.65 to -5.10 eV as the electrondonating ability increases with the size of the bridged oligothiophene going from 1T to 6T. The LUMO level is held constant at -3.84 eV. This is because the highly twisted conformation between the bridged-oligothiophene and terminal pervlene chromophoric unit significantly reduced the electron conjugation between them, and hence the LUMO energy is mainly determined by the electron-accepting perylene and the HOMO energy is, however, mainly related to the oligothiophene. This is indicated by the nearly identical absorption band from the oligothienyl bridge of the PDI dimer (Figure 4(a)) to that of the corresponding oligothiophene (Figure S3), both in the solution state. The



Figure 3 (a) Cyclic voltammograms of the six PDI dimers in DCM with 0.1 mol/L Bu_4NPF_6 . Scan rate was 100 mV/s, Ag/AgCl was used as reference electrode; (b) energy diagram of P3HT, $PC_{61}BM$ and the six PDI dimers.



Figure 4 UV-Vis absorption spectra of the six PDI dimers in a dilute DCM with a concentration of 1×10^{-6} mol/L (a) and in thin films on the quartz plates (b).

electrochemical band gaps (E_g^{cv}) are estimated from the CV data and listed in Table 1. The band gap decreases from 1.81 to 1.26 eV. The HOMO and LUMO levels of the PDI dimers are both lower than those of P3HT, allowing for the use as the acceptor material.

3.6 Absorption spectra

Figure 4(a) displays the absorption spectra of the six PDI dimers of **1T–6T** in dilute DCM solutions, and the optical properties are shown in Table 2. The oligothiophene segments **2c–2f** are chosen for comparison (Figure S3 and Table S1). **1T–6T** all show two well-separated absorption

Table 2Optical properties of the six PDI dimers

	S	olution	Film		
PDI	$\lambda_{\max}(nm)$	$\varepsilon_{max}/10^3 (L/(mol \ cm))$	λ_{\max} (nm)	$\lambda_{onset}(nm)$	
1T	530, 562	51.0, 56.4	522, 645	732	
2 T	362, 514, 566	39.8, 53.9, 54.8	338, 524, 572	752	
3 T	397, 523, 562	53.7, 58.0, 46.0	398, 528, 568	785	
4 T	404, 535, 562	56.8, 59.6, 47.4	415, 541, 580	821	
5T	421, 536	63.4, 58.1	432, 542, 662	838	
6T	432, 536	70.5, 58.0	472, 560, 671	862	

bands (indicating by the dashed green arrow): the right one is mainly benefited from the PDI chromophores and originated from its electronic $S_0 \rightarrow S_1$ transition (B_{PDI}), whereas the left one is mainly from the bridged oligothiophene (B_T) segment. The absorptivity of the B_T increases with the increase of the size and its peak red-shifts simultaneously. The maximum extinction coefficient of the B_{PDI} is 55×10^3 - 60×10^3 L/(mol cm) for all the dimers. While, its shape varies with the bridge size. 1T exhibits two absorption peaks around 530 and 562 nm, respectively. Their intensity is close to each other. 2T shows a broader band with two peaks at 514 and 566 nm. The intensity of these two peaks is identical. 3T-6T, however, gives a hypochromically shifting peak at 523 nm for 3T and around 535 nm for 4T-6T. The lift of the long-wavelength edge of the B_{PDI}, as observed from 2T-6T in between 600–700 nm, is due to the intramolecular charge-transfer (ICT) transition from the electron-donating oligothiophene to the electron-accepting PDI unit.

As the dimer transitions from the dilute solution to the thin film, the absorption band of B_{PDI} is broadened obviously towards the long-wavelength and, for example, there appears an apparent shoulder around 645 nm for **1T** and a visible band around 700 nm for **6T**, as shown in Figure 4(b). The long-wavelength edge of the B_{PDI} (λ_{onset}) extends to 732, 752, 785, 821, 838 and 862 nm for **1T–6T**, respectively. The estimated optical bandgap from the λ_{edge} is in line with that from the electrochemical data. Conspicuously, the larger bridge size leads to a more red-shifted absorption band and a lower bandgap. The band of B_{T} of **5T** and **6T** becomes much stronger than that of B_{PDI} and the B_{T} Peak of **T6** is bathochromatically shifted from 432 nm in solution to 472 nm in film.

3.7 Photovoltaic property

The photovoltaic property of the PDI dimer was primarily characterized by selecting the commercial P3HT as the blend donor. The solution-processed bulk-heterojunction (BHJ) solar cells were fabricated with a conventional configuration of ITO glass/PEDOT:PSS/P3HT:PDI dimer/Ca/Al and were tested under an AM 1.5G simulated solar light at 100 mW/cm². Here, PEDOT:PSS is poly (3,4-ethylenedioxy thiophene):poly (styrenesulfonate). Table S1

collects the photovoltaic data under various optimizing conditions. The best D:A weight ratio is of 1:1. The host solvent is 1,2-dichlorobenzene (*o*-DCB).

Treatment of the 1:1 (*w*/*w*) blend film of P3HT:**1T** by following a solvent vapor annealing or a thermal annealing process gives a PCE of 0.89% and 0.47%, respectively (Table S1). As the annealing process is applied firstly with the solvent vapor annealing and followed by the thermal annealing, a higher PCE of 1.16% is obtained with a shortcircuit current-density (J_{sc}) of 3.18 mA/cm², an open-circle voltage (V_{oc}) of 0.57 V, and a fill factor (FF) of 64.3%. The optimal processing conditions for **1T** were then applied for other PDI dimers. Table 3 collects the photovoltaic parameters of the best cells and Figure 5 displays the representative current density-voltage (*J-V*) curves. Among the six PDI dimers, **1T**, **4T** and **6T** gives a PCE higher than 1%, whereas another three have a PCE lower than 0.5%. The low J_{sc} is a major factor for the low PCE.

The accuracy of the *J*-*V* measurement is confirmed by the EQE spectra (Figure 6(a)) of the best cells. The EQE responses cover a wide wavelength range from 350 to 700 nm, and match with the corresponding absorption spectrum of the blend film (Figure 6(b)). The shoulder before 500 nm, for example, that around 410, 440 and 500 nm for **3T**, **4T** and **6T** indicates the contributions from the PDI dimer, particularly, from the oligothienyl bridge, to the photon-to-

Table 3 Photovoltaic parameters of the best cells using P3HT as theblend donor

PDI	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE	(%)	$\mu_{ m e}$
	(V)	(mA/cm^2)	(%)	Best	av. ^{a)}	$10^{-5} (cm^2/(Vs))$
1T	0.57	3.18	64.3	1.16	1.10	72
2 T	0.64	1.15	52.6	0.38	0.34	15
3T	0.38	1.50	44.4	0.25	0.20	5.3
4T	0.66	2.76	59.7	1.08	0.98	57
5T	0.51	0.66	32.5	0.11	0.10	1.7
6T	0.62	4.57	44.2	1.26	1.18	39

a) av.=average value, estimated from 10 devices.



Figure 5 The *J*-*V* curves of the best devices based on the 1:1 blended film of P3HT and PDI dimer.



Figure 6 (a) EQE curves of the best cells; (b) absorption spectra of 1:1 (w/w) blend films with **1T–6T** as the acceptor.

electron conversion. The lift of the EQE tail between 650 and 800 nm, for example, as observed from **6T**, further supports the contribution from the PDI acceptor. These current density integrated from the EQE spectrum is 2.91, 1.07, 1.38, 2.55, 0.61, 4.20 mA/cm² for **1T–6T**, respectively, which is in good agreement with the J_{sc} values (Table 3).

The V_{oc} is generally related to the energy difference between the LUMO of the acceptor and the HOMO of the donor. Otherwise, it is also affected by the film-morphology. As we have observed that the V_{oc} is raised with the increase of the phase size [22]. The V_{oc} value is about 0.60 V for the dimer of **1T**, **2T**, **4T** and **6T**, respectively, which is close to the value reported from other systems of P3HT:PDI dimer [21,28]. These four dimers has a solubility value of about or larger than 20 mg/mL (Table 1). Good quality blend films can be obtained from these dimers. However, **3T** and **5T** has a much smaller solubility, only about 9 mg/mL. Indeed, we observed that the blend film from these two dimers is worse than that from other four dimers. In fact, the filmquality dependent V_{oc} is a normal phenomenon in the fabrication of organic solar cells.

3.8 Electron mobilities

The electron mobilities were carried out by the SCLC method with an electron-only device of ITO/TIPD/active layer/Al. Figure S4 shows the plots of $\ln(JL^3/V^2)$ vs. $(V/L)^{0.5}$, which are extracted from the experimental electron-only *J*-*V* data, and Table 3 gives the estimated electron mobilities. The solar cell blend of P3HT:**1T**, P3HT:**4T**, and P3HT:**6T** each shows a higher electron mobility, while each of P3HT:**4T** and P3HT:**6T** has a much lower electron mobility. The change trend of the electron mobility is in accordance with the varying tendency of the J_{sc} .

3.9 Film-morphology

The film-morphology of the solar cell blend was character-

ized with TEM, as shown in Figure 7. The blend film from **1T**, **2T**, **4T** and **6T** each shows nanoscale interpenetrating networks with smaller phase size, and the white/black domain size if of 20/30, 35/65, 35/50, 35/50 nm, respectively. In contrast, each of **3T** and **5T** gives much different filmmorphology with relatively larger phase size (>100 nm).

4 Conclusions

Except for the reported dimer of 1T, another five new PDI dimers were successfully synthesized by using oligothiephene as the covalent aromatic bridge. The bridged oligothiophene segment shows an absorption band before 500 nm, which is complementary to that of the covalent PDI chromophore. The ICT absorption from the electrondonating oligothiophene segment to the electron-accepting PDI unit enhances with the increase of the oligothienyl size, leading to a raise of absorption in the near IR region from 650 to 900 nm. Therefore, the absorption from the oligothienyl, PDI chromophore and the ICT between oligothienyl and PDI together contributes to a wide spectral coverage from 350 to 900 nm. The HOMO level increases from -5.65 to -5.10 eV as the size of the oligothiophene increases, while, the LUMO level is held constant at -3.84 eV. This leads to a decrease of the band gap going from 1.81 to 1.26 eV as the covalent bridge goes from 1T to 6T. Taken together, a series of low bandgap and wide spectral coverage small molecule acceptors are reported. The photovoltaic property of each dimer is checked using P3HT as the donor, while the dimer as the non-fullerene acceptor.

Although the PCE from non-fullerene organic acceptor based solution-processed solar cells has been raised over 6%, this value is still yet largely lagged from the fullerenebased counterparts, from which a PCE of 10%–11% has been reported from several donor-acceptor systems with a single-junction solution-processed device structure [45–48].



Figure 7 TEM images of the solar cell films based on 1:1 blended P3HT and **1T** (a), or **2T** (b), or **3T** (c), or **4T** (d), or **5T** (e), or **6T** (f), respectively, fabricated under the optimal conditions of the best cells.

Therefore, efforts on the design and synthesis of new organic acceptors and understanding of the reasons between the performance differences should be made to further improve the electric property of the non-fullerene organic solar cells.

Acknowledgments This work was supported by the National Natural Science Foundation of China (21327805, 91227112, 91433202, 21221002), Chinese Academy of Sciences (XDB12010200), Ministry of Science and Technology of China (2011CB808400, 2013CB933503, 2012YQ120060).

Conflict of interest The authors declare that they have no conflict of interest.

Supporting information The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

- 1 Tang CW. Appl Phys Lett, 1986, 48: 183-185
- 2 Brunetti FG, Gong X, Tong M, Heeger AJ, Wudl F. Angew Chem Int Ed, 2010, 49: 532–536
- 3 Holcombe TW, Norton JE, Rivnay J, Woo CH, Goris L, Piliego C, Griffini G, Sellinger A, Bredas JL, Salleo A, Fréchet JM. J Am Chem Soc, 2011, 133: 12106–12114
- 4 Bloking JT, Han X, Higgs AT, Krastrop JP, Pandey L, Norton JE, Risko C, Chen CE, Brédas JL, McGehee MD, Sellinger A. *Chem Mater*, 2011, 23: 5484–5490
- 5 Ahmed E, Ren G, Kim FS, Hollenbeck EC, Jenekhe SA. *Chem Mater*, 2011, 23: 4563–4577
- 6 Ren G, Ahmed E, Jenekhe SA. Adv Energy Mater, 2011, 1: 946–953
- 7 Wang X, Huang JH, Niu ZX, Sun YX, Zhan CL. Tetrahedron, 2014, 70: 4726–4731
- 8 Fernando R, Mao Z, Muller E, Ruan F, Sauvé G. J Phys Chem C, 2014, 118: 3433–3442
- 9 Zhou TL, Jia T, Kang BN, Li FH, Fahlman M, Wang Y. Adv Energy Mater, 2011, 1: 431–439
- 10 Zhou Y, Ding L, Shi K, Dai YZ, Ai N, Wang J, Pei J. Adv Mater, 2012, 24: 957–961
- 11 Zhou Y, Dai YZ, Zheng YQ, Wang XY, Wang JY, Pei J. Chem Commun, 2013, 49: 5802–5804
- 12 Pho TV, Toma FM, Chabinyc ML, Wudl F. Angew Chem Int Ed, 2013, 52: 1446–1451
- 13 Lin YZ, Li YF, Zhan XW. Adv Energy Mater, 2013, 3: 724–728
- 14 Shu Y, Lim YF, Li Z, Purushothaman B, Hallani R, Kim JE, Parkin SR, Malliaras GG, Anthony JE. *Chem Sci*, 2011, 2: 363–368
- 15 Winzenberg KN, Kemppinen P, Scholes FH, Collis GE, Shu Y, Singh TB, Bilic A, Forsythb CM, Watkins SE. *Chem Commun*, 2013, 49: 6307–6309
- 16 Zhan CL, Li ADQ. Curr Org Chem, 2011, 15: 1314–1339
- 17 Schmidt R, Oh JH, Sun YS, Deppisch M, Krause AM, Radacki K, Braunschweig H, Könemann M, Erk P, Bao ZN, Würthner F. J Am Chem Soc, 2009, 131: 6215–6228
- 18 Zhao Y, Guo YL, Liu YQ. Adv Mater, 2013, 25: 5372-5391
- 19 Würthner F. Chem Commun, 2004: 1564–1579

- 20 Rajaram S, Armstrong PB, Kim BJ, Fréchet JMJ. Chem Mater, 2009, 21: 1775–1777
- 21 Lu ZH, Zhang X, Zhan CL, Jiang B, Zhang XL, Chen LL, Yao JN. *Phys Chem Chem Phys*, 2013, 15: 11375–11385
- 22 Zhang X, Lu ZH, Ye L, Zhan CL, Hou JH, Zhang SQ, Jiang B, Zhao Y, Huang JH, Zhang SL, Liu Y, Shi Q, Liu YQ, Yao JN. Adv Mater, 2013, 25: 5791–5797
- 23 Jiang B, Zhang X, Zhan CL, Lu ZH, Huang JH, Ding XL, He SG, Yao JN. *Polym Chem*, 2013, 4: 4631–4638
- 24 Yan QF, Zhou Y, Zheng YQ, Pei J, Zhao DH. Chem Sci, 2013, 4: 4389–4394
- 25 Jiang W, Ye L, Li XG, Xiao CY, Tan F, Zhao WC, Hou JH, Wang ZH. *Chem Commun*, 2014, 50: 1024–1026
- 26 Shivanna R, Shoaee S, Dimitrov S, Kandappa SK, Rajaram S, Durrant JR, Narayan KS. *Energy Environ Sci*, 2014, 7: 435–441
- 27 Lin YZ, Wang JY, Dai SX, Li YF, Zhu DB, Zhan XW. Adv Energy Mater, 2014, 4: 1400420
- 28 Zhang X, Yao JN, Zhan CL. Chem Commun, 2015, 51: 1058–1061
- 29 Lin YZ, Wang YF, Wang JY, Hou JH, Li YF, Zhu DB, Zhan XW. *Adv Mater*, 2014, 26: 5137–5142
- 30 Zhang X, Jiang B, Zhang SQ, Hou JH, Yao JN, Zhan CL. *Proc SPIE*, 2014, 9184: 91840C
- 31 Sharenko A, Proctor CM, van der Poll TS, Henson ZB, Nguyen TQ, Bazan GC. Adv Mater, 2013, 25: 4403–4406
- 32 Ye TL, Singh R, Butt HJ, Floudas G, Keivanidis PE. ACS Appl Mater Inter, 2013, 5: 11844–11857
- 33 Singh R, Aluicio-Sarduy E, Kan Z, Ye TL, MacKenzie RCI, Keivanidis PE. J Mater Chem A, 2014, 2: 14348–14353
- 34 Zhang XL, Jiang B, Zhang X, Tang AL, Huang JH, Zhan CL, Yao JN. *J Phys Chem C*, 2014, 118: 24212–24220
- 35 Lu ZH, Jiang B, Zhang X, Tang AL, Chen LL, Zhan CL, Yao JN. *Chem Mater*, 2014, 26: 2907–2914
- 36 Zang Y, Li CZ, Chueh CC, Williams ST, Jiang W, Wang ZH, Yu JS, Jen AKY. Adv Mater, 2014, 26: 5708–5714
- 37 Zhong Y, Trinh MT, Chen RS, Wang W, Khlyabich PP, Kumar B, Xu QZ, Nam CY, Sfeir MY, Black C, Steigerwald ML, Loo YL, Xiao SX, Ng F, Zhu XY, Nuckolls C. J Am Chem Soc, 2014, 136: 15215–15221
- 38 Zhang X, Zhan CL, Yao JN. Chem Mater, 2015, 27: 166–173
- 39 Zhao JB, Li YK, Lin HR, Liu YH, Jiang K, Mu C, Ma TX, Lai JYL, Yan H. *Energy Environ Sci*, 2015, 8: 520–525
- 40 Lin YZ, Wang JY, Zhang ZG, Bai HT, Li YF, Zhu DB, Zhan XW. Adv Mater, 2015, 27: 1170–1174
- 41 Tan ZA, Zhang WQ, Zhang ZG, Qian DP, Huang Y, Hou JH, Li YF. *Adv Mater*, 2012, 24: 1476–1481
- 42 An ZS, Yu JS, Jones SC, Barlow S, Yoo S, Domercq B, Prins P, Siebbeles LDA, Kippelen B, Marder SR. Adv Mater, 2005, 17: 2580– 2583
- 43 Zhang X, Pang SF, Zhang ZG, Ding XL, Zhang SL, He SG, Zhan CL. Tetrahedron Lett, 2012, 53: 1094–1097
- 44 Zhang X, Zhan CL, Zhang XL, Yao JN. *Tetrahedron*, 2013, 69: 8155–8160
- 45 Li YF. Sci China Chem, 2015, 58: 188
- 46 Wu HB. Sci China Chem, 2015, 58: 189
- 47 Huang F. Sci China Chem, 2015, 58: 190
- 48 Li YF. Sci China Chem, 2015, 58: 191